

AlN SINTERED COMPACT AND PRODUCTION THEREOF

Patent Number: JP6219844
Publication date: 1994-08-09
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Requested Patent: ☐ JP6219844
Application Number: JP19930011740 19930127
Priority Number(s):
IPC Classification: C04B35/58
EC Classification:
Equivalents:

Abstract

PURPOSE:To improve heat conductivity and thermal fatigue resistance by specifying the intercrystalline boundary phase composition of cutting plane of an AlN sintered compact.

CONSTITUTION:The AlN sintered compact 0.1-15μm in average circumferential length of the intercrystalline boundary phase of the sintered compact cutting plane, 0.5-1.0 in the ratio of average minimum diameter to average maximum diameter, ≤ 0.5 in the ratio of average particle diameter to that of AlN grain and having $3Y_2O_3 \cdot 5Al_2O_3$ and $Y_2O_3 \cdot Al_2O_3$ in the intercrystalline boundary phase composition is obtained by mixing a powdery AlN raw material $\geq 95\%$ in purity, $\leq 20\mu m$ in average particle diameter, $\leq 500ppm$ in metallic impurities content and $\leq 4wt. \%$ in oxygen content with a sintering assistant of the oxide or carbonate of Y so as to be $4.73b-6.30c > a > 2.81b-3.75c$ when the adding quantity of the sintering assistant is (a) wt.% expressed in terms of oxide Y_2O_3 , oxygen contained in an oxygen containing modifying agent and the powdery AlN raw material after degreasing is (b) wt.% and carbon contained in the molding after degreasing is (c) wt.% and degreasing and sintering after adding 3-15wt.% organic binder and molding.

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6-219844

[Title of the Invention]

AlN Sintered Body and Production Method Thereof

[Abstract]

[Object]: To provide an AlN sintered body excellent in a heat fatigue resistance while keeping a high thermal conductivity.

[Constitution]: An AlN sintered body controlled to have a specified structure of grain boundary phase with a composition consisting of YAG phase and YAP phase.

[Claims]

1. An AlN sintered body containing grain boundary phase, wherein the grain boundary phase in a cross-sectional face of the sintered body has:

- (a) an average circumferential length of 0.1 to 15 μm ;
- (b) the ratio of the average minimum particle size and the average maximum particle size of 0.5 to 1.0; and
- (c) the ratio of the average particle size and the average particle size of AlN particles of 0.5 or less, and
the grain boundary phase composition includes $3\text{Y}_2\text{O}_3\text{-}5\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$.

2. A production method of an AlN sintered body, wherein when an addition amount of a sintering aid is "a" wt.% in terms of

oxide Y_2O_3 , an amount of oxygen contained in an oxygen content adjusting agent and AlN raw material powder after degreasing is "b" wt.% and an amount of carbon contained in a formed body after degreasing is "c" wt.% in a sintering aid of Y oxide and/or carbonate, the sintering aid is mixed with an AlN raw material powder, and the mixture is formed and fired so as to satisfy the following inequality:

$$4.73b - 6.30c > a > 2.81b - 3.75c.$$

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an AlN sintered body with high-thermal conductivity and excellent heat fatigue resistance characteristics.

[0002]

[Prior Art]

Recently, owing to the rapid technical innovation in semiconductor industries, progress in high integration and high output power of large scale integration circuits such as ICs and LSIs is remarkable and with such a trend, the heat generation quantity per a package is rapidly increased, and therefore, the heat releasing property of a substrate material is considered to be important and beryllia that is excellent in the thermal conductivity is partially used as a substrate material in place of alumina; however, beryllia is highly toxic and problematic for handling. Consequently, as a substrate material substituting for alumina and beryllia, AlN is now drawing attention.

[0003]

A variety of applications with respect to sintered bodies using such as sintering aids for AlN sintered bodies and methods for their production have been applied and especially, in recent years, applications relevant to the methods for producing AlN sintered bodies with high-thermal conductivity and the structures and compositions of the grain boundary phases of the sintered bodies (e.g., JP Kokai Sho 62-52181, JP Kokai Sho 62-171964, JP Kokai Hei 2-38369 and the like). Further, the microstructures affecting the thermal conductivity of AlN sintered bodies have been investigated [24th Resume of Basic Discussion on Ceramics, p.175 (1986), Journal of Ceramics 97 [12], 1478 (1989)]. Further, a finding with respect to a sintered body produced by using $\text{Ca}(\text{NO}_3)_2$ as a sintering aid that the grain boundary phases including sintering aid components are found to be spherical is disclosed in Journal of Ceramics 93[9], 41 (1985).

[0004]

[Problems to be Solved by the Invention]

As described above, an AlN sintered body disclosed recently shows excellent thermal conductivity; however, when the heat generation quantity is increased attributed to high output power and high integration trend, the heat fatigue resistance such as heat cycle resistance property and the like becomes difficult to be assured and cracking takes place in a thin plate such as a substrate to result in a problem in a substrate circuit. Therefore, it is required to improve the heat resistance cycle property and it is an object of the invention to improve such a property.

[0005]

[Means for Solving the Problems]

The present inventors have made a variety of investigations in order to solve the above-mentioned problems and have found an AlN sintered body containing grain boundary phase, wherein the grain boundary phase in a cross-sectional face of the sintered body has: (a) an average circumferential length of 0.1 to 15 μm ; (b) the ratio of the average minimum particle size and the average maximum particle size of 0.5 to 1.0; and (c) the ratio of the average particle size and the average particle size of AlN particles of 0.5 or less, and the grain boundary phase composition includes $3\text{Y}_2\text{O}_3\text{-}5\text{Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$, and a production method of an AlN sintered body, wherein when an addition amount of a sintering aid is "a" wt.% in terms of oxide Y_2O_3 , an amount of oxygen contained in an oxygen content adjusting agent and AlN raw material powder after degreasing is "b" wt.% and an amount of carbon contained in a formed body after degreasing is "c" wt.% in a sintering aid of Y oxide and/or carbonate, the sintering aid is mixed with an AlN raw material powder, and the mixture is formed and fired so as to satisfy the following inequality: $4.73b - 6.30c > a > 2.81b - 3.75c$.

[0006]

Herein, when the structure of the AlN sintered body using the sintering aid is observed, "grain boundary phases" as liquid phases obtained by which the sintering aid solidifies "AlN (crystal) grains" as oxide are covered on the AlN sintered body; however, the present inventors have found that a covering manner of the grain boundary phases and a state of existence of the grain boundary phases effect the thermal conductivity of the AlN sintered body and, also, is associated with the heat fatigue resistance

property such as heat resistant property of the AlN sintered body.

[0007]

As a result of the analysis of the AlN sintered body, it has been found that the heat fatigue resistance property of the AlN sintered body can be improved while the high-thermal conductivity being maintained by limiting the shape, size and composition of the grain boundary phases. That is, it has been found that in such an AlN sintered body, the grain boundary phases are small and spherical, and have a composition consisting of $3Y_2O_3 \cdot 5Al_2O_3$ (hereinafter, abbreviated as YAG) and $Y_2O_3 \cdot Al_2O_3$ (hereinafter, abbreviated as YAP).

[0008]

The present inventors have found that an AlN sintered body excellent in the heat fatigue resistance property while keeping a high-thermal conductivity can be obtained by providing the following characteristics quantified as an average circumferential length in a cross-sectional face of grain boundary phases of the AlN sintered body is 0.1 to 15 μm ; the ratio of the average minimum particle size and the average maximum particle size is in 0.5 to 1.0; and the ratio of the average particle size and the average particle size of AlN particles is 0.5 or less and that the grain boundary phase composition includes YAG and YAP.

[0009]

When the average circumferential length in a cross-sectional face of grain boundary phases of the AlN sintered body exceeds 15 μm , the contact surface area with the AlN crystals becomes too high and significant cracking easily takes place in the grain boundary phases to result in deterioration of

heat fatigue resistance property of the sintered body and when it is less than $0.1\text{ }\mu\text{m}$, the thermal conductivity is adversely decreased. Also, when the ratio of the average minimum particle size and the average maximum particle size is less than 0.5 or the ratio of the average particle size and the average particle size of AlN particles exceeds 0.5, similarly significant cracking easily takes place in the grain boundary phases to result in deterioration of heat fatigue resistance property of the AlN sintered body. In the present invention, the grain boundary phases of the AlN sintered body exist in spherical state in grain boundaries and triple points and, thus, the size of the grain boundary phases and the contact surface area of the grain boundary phases with the AlN particles are extremely small.

[0010]

Next, a production method of a sintered body of the present invention will be sequentially described in order of the steps and with respect to the factors other than the addition amount of a sintering aid and the relation of mixing ratios of oxygen amounts of an oxygen content adjusting agent and the like, that is, an AlN fine powder raw material, a binder and a raw material mixing method, a forming method, degreasing and sintering methods, manners, and their conditions are as those employed conventionally.

[0011]

As an AlN fine powder to be used as a main raw material, those with a purity of 95% or more, an average particle size of $20\text{ }\mu\text{m}$ or less, preferably $5\text{ }\mu\text{m}$ or less, a metal impurity content of 500 ppm or less, and an oxygen content of 4 wt.% or less are preferable. As a sintering aid that performs

an important role in the present invention, Y oxide and/or carbonate is used. When an addition amount of a sintering aid is "a" wt.% in terms of oxide Y_2O_3 , an amount of oxygen contained in an oxygen content adjusting agent and AlN raw material powder after degreasing is "b" wt.% and an amount of carbon contained in a formed body after degreasing is "c" wt.% in a sintering aid of Y oxide and/or carbonate, the sintering aid is mixed with an AlN raw material powder, and the mixture is formed and fired so as to satisfy the following inequality: $4.73b - 6.30c > a > 2.81b - 3.75c$ and, in some cases, the oxygen content adjusting agent is mixed within the range which satisfies the above-mentioned inequality. The meaning of "after degreasing" will be described later.

[0012]

The addition amount of the sintering aid of the present invention is important to satisfy the above-mentioned inequality and preferably 2 to 10 wt.%, more preferably 2 to 7 wt.%, in the total weight of the AlN raw material powder, the sintering aid and the oxygen content adjusting agent. When it is less than 2 wt.%, it takes a long time to obtain a dense sintered body and when it exceeds 10 wt.%, the thermal conductivity is decreased.

[0013]

The oxygen content adjusting agent in the present invention means an additive to be added so as to adjust the oxygen amount relevant to the above-mentioned inequality and alumina, Al_2O_3 , an oxide of aluminum or an oxynitride of alumina may be used. When the above-mentioned inequality is satisfied and oxygen contained in the AlN raw material powder is sufficient, it is no need to add the oxygen content adjusting agent of such as

alumina or the like.

[0014]

Further, when carbon is contained in a formed body before sintering, reaction with oxygen contained in the AlN raw material powder is caused, so that the addition amount of the sintering aid should be decreased or the above-mentioned addition amount of the oxygen content adjusting agent of such as alumina should be increased for the present invention.

[0015]

An AlN fine powder and a sintering aid are mixed by dry mixing manner or wet mixing manner using an organic solvent and the latter wet mixing manner is preferable since mixing can be well carried out. The mixed powder is further mixed with 3 to 15 wt.%, preferably 5 to 10 wt.%, of an organic binder such as a paraffin wax, polyvinyl butyral, ethylcellulose and the like and formed into a prescribed shape by proper forming means, for example, by a dry pressing method, a rubber pressing method, an injection method, an extrusion method, a doctor blade sheet forming method and the like. In the case of a die molding method, it is general to use a granulated powder. Also, in the case of an AlN sintered substrate, generally, a doctor blade method is employed for forming. In this case, it is common to mix an organic solvent, a dispersant of such as polyethylene glycol or the like, a binder of such as polyvinyl butyral, a plasticizer of such as butyl phtharylbutyl glycolate with an AlN raw material powder and a sintering aid, and form a thin raw sheet (a green sheet) from the mixture by the doctor blade method.

[0016]

After forming, the formed body is subjected to degreasing treatment at 400 to 700°C in vacuum, N₂, Ar or atmospheric air for 0.1 to 24 hours. In the present invention, "the carbon amount contained in a formed body after degreasing" in the case the amount of a sintering aid to be added is defined means the total carbon amount contained in an obtained formed body after a formed body subjected to the foregoing degreasing treatment is heated at 1300°C for 2 hours in non-oxidizing atmosphere or in vacuum. The carbon amount is preferably 2 wt.% or less. Also, "the oxygen content contained in the oxygen content adjusting agent and the AlN raw material powder after degreasing" means the total oxygen amount contained in the AlN raw material powder and the oxygen content adjusting agent when both are at first heated at 400 to 700°C in vacuum, N₂, Ar or atmospheric air for 0.1 to 24 hours and successively heated at 1300°C for 2 hours in non-oxidizing atmosphere or in vacuum.

[0017]

After degreasing, sintering is carried out at 1700 to 2000°C for 0.1 to 24 hours in -500 mmHg to 10 kg/cm² in vacuum or a non-oxidizing gas such as N₂, Ar or the like. The grain boundary phases covering the AlN (crystals) grains of the AlN sintered body of the present invention obtained in such a manner as to exist in spherical form in grain boundaries or triple points and thus the size of the grain boundary phases and the contact surface area of the AlN grains with the grain boundary phases are extremely small.

[0018]

Further, the grain boundary phases containing the sintering aid

components of the AlN sintered body of the invention consist of YAG having a garnet type crystal structure and YAP having a perovskite type crystal structure. The quantitative ratio of them is preferably in a range satisfying the following: $0.1 < I(\text{YAG})/I(\text{YAP}) < 3$ wherein $I(\text{YAG})$ denotes the diffraction peak of YAG phase in plane index (5 3 2) at diffraction angle $2\theta = 46.6^\circ$ and $I(\text{YAP})$ denotes the diffraction peak of YAP phase in plane index (1 2 1) at diffraction angle $2\theta = 34.3^\circ$ in observation by comparison of peaks of powder x-ray diffraction (Cu $K\alpha$: 40 Kv, 20 mA; scanning speed of 1 dcg/min) and in this case, the addition amount a wt.% of the sintering aid is preferably within a range satisfying: $4.31b - 5.75c > a > 2.88b - 3.83c$. The "a", "b" and "c" in the inequality are same as defined above. With respect to the YAG phase and the YAP phase, when the oxygen amount contained in the aluminum nitride raw material powder is high as compared to the addition amount of the sintering aid of such as yttrium oxide, the YAG phase tends to be increased and the YAP phase tends to be decreased and in the opposed case, the YAG phase tends to be decreased and the YAP phase tends to be increased.

[0019]

[Examples]

Hereinafter, the present invention will be described with reference to examples.

Example 1

At first, the contained oxygen amount and the contained carbon amount in a formed body after degreasing specifically defined in the present invention were measured in an AlN raw material powder to be used for

sintering. That is, 1 part by weight of polypropylene glycol and 5 parts by weight of polyvinyl butyral as binders for forming, 5 parts by weight of dibutyl phthalate as a plasticizer, and 27 parts by weight of butanol as a solvent were added to 100 parts by weight of a commercially available AlN raw material powder by an Al direct nitridation method (oxygen content: 1.1 wt.%, average particle size: 1.5 μm , Fe: 60 ppm, Si: 100 ppm, Mg: <30 ppm) and mixed by a ball mill pot made of nylon for 48 hours to prepare a slurry. After being vacuum defoamed, the slurry was formed into a sheet-like formed body by a doctor blade method and dried. The obtained sheet with a thickness of 0.75 mm was punched out into a 30 mm square shape and subjected to degreasing at 550°C for 6 hours in atmosphere. The degreased sheet was further heated at 1300°C for 2 hours in nitrogen. The contained oxygen amount and the contained carbon amount in the heated formed body were found to be 1.4 wt.% and 0.04 wt.%, respectively. In this case, no oxygen content adjusting agent was added and polypropylene glycol and the like other than the AlN raw material powder was confirmed not to leave oxygen at 1300°C; therefore, the contained oxygen amount in the formed body after degreasing was equivalent as it is to the oxygen amount b wt.% contained in the oxygen content adjusting agent (in Example 1, not added) and an AlN raw material powder after degreasing as defined in the present invention.

[0020]

Next, the same amounts of the binders for forming, the plasticizer, and the solvent all same as those described above were added to 100 parts by weight of a mixed powder of the same AlN raw material powder mixed

with about 5 wt.% of Y_2O_3 (an ultrafine powder product manufactured by Nippon Yttrium Co., purity: 99.9%, average particle size: 0.4 μm) and a green sheet with a thickness of 0.75 mm was produced by a similar method. The obtained sheet was punched out into a 30 mm square shape and subjected to degreasing at 550°C for 6 hours in atmosphere. After the degreasing, 10 degreased sheets obtained in such a manner as to be coated with boron nitride fine powder, laminated on one another, housed in a container made of boron nitride and sintered at 1830°C for 16 hours in nitrogen current (N_2 gas flow rate: 100 L/hr) under atmospheric pressure in a vacuum sintering furnace. In order to observe the structure or the like of the obtained sintered body, the sintered body was cut and the cut cross-section was polished and “the average circumferential length”, “the ratio of the average minimum particle size and the average maximum particle size” and “the ratio of the average particle size of the grain boundary phases and the average particle size of AlN particles” in the grain boundary phases of the sintered body were measured.

[0021]

It was found that “the ratio of the average minimum particle size and the average maximum particle side” in the grain boundary phases was smaller than 0.5. That is, the shape of the grain boundary phases was found not to be spherical; therefore, sintering was carried out again at 1825°C for 16 hours in nitrogen current. The structure of the obtained sintered body was evaluated by similar methods and the results are shown in Table 1. Further, each sintered body was finely pulverized to obtain a sample for powder x-ray diffraction to measure the $I(YAG)/I(YAP)$ value.

The apparatus employed for the measurement was Geigerflex RAD-2B manufactured by Rigaku Corporation and the main measurement conditions were as follows:

target	Cu K α ;
voltage, electric current	40 kV, 20 mA;
scanning speed	1 deg/min; and
slits	1-0.3-1.

[0022]

Next, the surface of each sintered body was subjected to wet blast treatment to remove the sintering aid deposited on the surface. Silicon carbide abrasive grains of #320 were used for the blast treatment. Using the substrate subjected to the surface blast treatment, a copper-clad substrate with a size shown in Fig. 1 was produced by the following method and subjected to heat fatigue resistance characteristic measurement. As a bonding material for the copper cladding, a paste-shaped material was prepared by mixing 15 wt.% of a vehicle of hexanol containing 12% of ethylcellulose with 85 wt.% of a metal powder mixture of 84.5 parts by weight of a Cu powder with a particle size of 5 to 20 μm , 14 parts by weight of a Ag powder with a particle size of 5 to 10 μm , and 1.5 parts by weight of a Ti powder with a particle size of 5 to 10 μm . The paste-shaped bonding material was applied in a thickness of 35 μm to each aluminum nitride sintered body by a screen printing method. In this case, the paste was applied only to the pattern portions in the circuit side and to the entire face of the heat sink in the heat sink side, respectively. Next, the coated aluminum nitride sintered body was dried and degreased at 600°C in profile

of 5 minutes and 30 minutes and a copper sheet was laminated to bond them by heating at 850°C for 5 minutes. Next, a resist was applied to the copper sheet surface in the circuit pattern side. The resist was applied by a screen printing method so as to wider by 200 μm than the circumference of the portions to be patterns. Further, the resist was applied to the entire face of the copper sheet in the heat sink side.

[0023]

After the resist application, a ferric chloride solution at 39°C was sprayed to remove the unnecessary copper sheet portions to which no resist was applied and washing with water and drying were carried out to obtain a copper-clad substrate. Then, the obtained copper-clad substrate was subjected to the heat fatigue resistance characteristic evaluation. The heat fatigue resistance evaluation test was carried out by employing a heating and cooling method of heating to 400°C in 10 minutes from a room temperature in nitrogen atmosphere; keeping at 400°C for 5 minutes; and then cooling to a room temperature. The number of the cycles until the cracking took place in the sintered body was investigated. As a result, the heat fatigue resistance characteristic was found excellent as compared with that of a conventional one (the results of heat fatigue resistance characteristic evaluation are shown in Table 1). Further, the voids in the sintered body were measured by boiling the sintered body in water for 3 hours and weighing the saturated water amount and the results are also shown together. The thermal conductivity of each sintered body subjected to the heat cycle test was measured by laser flash method and also shown in Table 1.

[0024]

Example 2

An AlN raw material powder was used which was obtained by pulverizing the AlN raw material powder with a purity of 99.9% same as that in Example 1 by a wet ball mill using alumina balls of 15 to 20 mm ϕ in an aqueous solvent to an average particle size of 1.1 μ m. In this case, the oxygen content b value after degreasing was 1.8 wt.% supposedly attributed to contamination with Al₂O₃. A sintered body was obtained in the entirely same conditions as those of Example 1, except that the above-mentioned point and the sintering temperature was 1820°C (the retention time was same, 16 hours). The results of the structure of the sintered body, I (YAG)/I (YAP) value, the heat fatigue resistance characteristic and the like were measured and shown in Table 1.

[0025]

Example 3

A sintered body was obtained in the entirely same conditions as those of Example 1, except that an un-pulverized AlN raw material powder with an oxygen content of 2.5 wt.% and the b value of 2.5 wt.% as well after degreasing (other average particle sizes and the impurity amounts were same as those of the raw material of Example 1) was used as the AlN raw material powder; the addition amount of Y₂O₃ was 6.2 wt.%; the degreasing conditions before sintering were at 680°C for 2 hours in vacuum (1×10^{-1} Torr); and the sintering temperature was 1825°C (the retention time was same, 16 hours). The characteristics and the like of the sintered body were shown in Table 1.

[0026]

Example 4

A sintered body was produced by the entirely same treatment as that of Example 3, except that the addition amount of Y_2O_3 was changed to be 5.8 wt.% and the characteristics and the like were obtained as shown in Table 1.

[0027]

Example 5

A sintered body was produced by the entirely same treatment as that of Example 3, except that the raw material used was an un-pulverized AlN raw material powder with an oxygen content of 1.6 wt.% and the b value of 1.6 wt.% as well after degreasing and the addition amount of Y_2O_3 was changed to be 3.3 wt.% and the results as shown in Table 1 were obtained.

[0028]

Example 6

A sintered body was obtained in the entirely same conditions as those of Example 3, except that a commercially available AlN raw material powder by a reducing nitridation method (having oxygen content: 1.1 wt.%, the average particle size: 1.4 μm , Fe: 60 ppm, Si: 30 ppm, Mg: <5 ppm) having the b value of 1.1 wt.% as well after degreasing; the addition amount of Y_2O_3 was 3.0 wt.%; and the sintering was carried out at 1825°C for 16 hours in nitrogen and further at 1805°C for 16 hours in nitrogen. The results shown in Table 1 were obtained. In the sintering stage at 1825°C for 16 hours, the obtained sintered body had the ratio of the average

minimum particle size and the average maximum particle size of 0.2 or less in the grain boundary phases, that is the particles of the sintered body include those which were not spherical and others with spherical shapes mixed together.

[0029]

Example 7

A sintered body was produced in the entirely same manner as that of Example 3, except that the addition amount of Y_2O_3 was changed to be 8.7 wt.% and a copper sheet was bonded to obtain a substrate. Then, the heat fatigue resistant characteristic of the substrate was evaluated in the same manner as that of Example 1. As a result, the heat fatigue resistance characteristic was found remarkably excellent unlike that of a conventional one (the results of the heat fatigue resistance characteristic evaluation are shown in Table 1).

Example 8

A sintered body was produced in the entirely same manner as that of Example 5, except that the addition amount of Y_2O_3 was changed to be 4.3 wt.% and a copper sheet was bonded to obtain a copper-clad substrate. Then, the heat fatigue resistant characteristic of the substrate was evaluated in the same manner as that of Example 1. As a result, the heat fatigue resistance characteristic was found remarkably excellent unlike that of a conventional one (the results of the heat fatigue resistance characteristic evaluation are shown in Table 1).

Example 9

A sintered body was produced in the similar manner to that of

Example 1, except that the addition amount of Y_2O_3 was changed to be 5.5 wt.% and a copper sheet was bonded to obtain a copper-clad substrate. Then, the heat fatigue resistant characteristic of the substrate was evaluated in the similar manner to that of Example 1. As a result, the heat fatigue resistance characteristic was found remarkably excellent unlike that of a conventional one (the results of the heat fatigue resistance characteristic evaluation are shown in Table 1).

[0030]

Example 10

A sintered body was produced in the similar manner to that of Example 3, except that the addition amount of Y_2O_3 was changed to be 5.3 wt.% and a copper sheet was bonded to obtain a copper-clad substrate. Then, the heat fatigue resistant characteristic of the substrate was evaluated in the similar manner to that of Example 1. As a result, the heat fatigue resistance characteristic was found remarkably excellent unlike that of a conventional one (the results of the heat fatigue resistance characteristic evaluation are shown in Table 1).

Example 11

A sintered body was produced in the similar manner to that of Example 3, except that the addition amount of Y_2O_3 was changed to be 8.5 wt.% and a copper sheet was bonded to obtain a copper-clad substrate. Then, the heat fatigue resistant characteristic of the substrate was evaluated in the similar manner to that of Example 1. As a result, the heat fatigue resistance characteristic was found remarkably excellent unlike that of a conventional one (the results of the heat fatigue resistance

characteristic evaluation are shown in Table 1).

[0031]

Example 12

As an oxygen content adjusting agent, 0.85 wt.% of a high purity alumina powder (purity: 99.9%, manufactured by Showa Denko K. K.) was added to 99.15 wt.% of the same aluminum nitride powder as that of Example 1. In this case, the b and c values after degreasing was 1.8 wt.% and 0.05 wt.%, respectively. The aluminum nitride powder mixed with the above-mentioned oxygen content adjusting agent was mixed with 6 wt.% of Y_2O_3 and formed, degreased, and sintered in the similar manner to that of Example 2 to obtain an aimed sintered body of the present invention. The precipitated agent phase in the surface of the obtained sintered body was removed and the heat fatigue resistant characteristic of a copper-clad substrate was evaluated in the similar manner to that of Example 1. As a result, the heat fatigue resistant characteristic was found excellent unlike that of a conventional one as shown in Table 1.

[0032]

Comparative Example 1

A sintered body was produced in the entirely same manner as that of Example 6, except that the addition amount of Y_2O_3 was changed to be 4.5 wt.% and the sintering temperature was changed to be 1805°C and the results shown in Table 1 were obtained.

Comparative Example 2

A sintered body was produced in the similar manner to that of Example 3, except that the addition amount of Y_2O_3 was changed to be 9.0

wt.%. Next, after the precipitated agent phase in the surface of the obtained sintered body was removed, the same paste-shaped bonding material as that of Example 1 was employed to bond a copper sheet and obtain a copper-clad substrate. Then, the heat fatigue resistant characteristic of the substrate was evaluated in the similar manner to that of Example 1. As a result, cracking took place in the sintered body in the first heating and cooling cycle to prove that the heat fatigue resistant characteristic was deteriorated (the results of the heat fatigue resistant characteristic evaluation are shown in Table 1).

[0033]

Comparative Example 3

A sintered body was produced in the similar manner to that of Example 3, except that the addition amount of Y_2O_3 was changed to be 9.5 wt.%. Next, after the precipitated agent phase in the surface of the obtained sintered body was removed, the same paste-shaped bonding material as that of Example 1 was employed to bond a copper sheet and obtain a copper-clad substrate. Then, the heat fatigue resistant characteristic of the substrate was evaluated in the similar manner to that of Example 1. As a result, cracking took place in the sintered body in the third heating and cooling cycle to prove that the heat fatigue resistant characteristic was deteriorated (the results of the heat fatigue resistant characteristic evaluation are shown in Table 1).

Comparative Example 4

A sintered body was produced in the similar manner to that of Example 3, except that the addition amount of Y_2O_3 was changed to be ~~9.5~~ 4.0

wt.% and the sintering temperature was changed to be $1850^{\circ}\text{C} \times 16 \text{ hr}$. Next, after the precipitated agent phase in the surface of the obtained sintered body was removed, the same paste-shaped bonding material as that of Example 1 was employed to bond a copper sheet and obtain a copper-clad substrate. Then, the heat fatigue resistant characteristic of the substrate was evaluated in the similar manner to that of Example 1. As a result, cracking took place in the sintered body in the third heating and cooling cycle to prove that the heat fatigue resistant characteristic was deteriorated (the results of the heat fatigue resistant characteristic evaluation are shown in Table 1).

[0034]

As being understood from the above-mentioned various results, those which maintained high thermal conductivity, and which showed good results in the heat cycle test were obtained in the examples but not obtained in the comparative examples.

[0036]

[Table 1]

	After degreasing		Y ₂ O ₃ addition amount (wt.%)	Average circumferential length of grain boundary phases (μm)	Ratio of (the average minimum particle size/the average maximum particle size) in grain boundary phases	Ratio of (the average particle size in grain boundary phase/the average particle size of AlN particles)	I (YAG)/YAP	AlN sintered body		
	Oxygen amount b (wt.%)	Carbon amount c (wt.%)						Porosity (%) -	Thermal conductivity (W/m·K)	Heat fatigue resistant characteristic cycle (times)
Example 1	1.4	0.04	5.0	6.1	0.89	0.28	1.11	< 1	161	18
Example 2	1.8	0.05	6.0	2.5	0.95	0.18	0.80	< 1	172	> 20
Example 3	2.5	0.48	6.2	4.7	0.92	0.24	0.40	< 1	167	> 20
Example 4	2.5	0.48	6.8	4.7	0.95	0.27	2.50	< 1	155	> 20
Example 5	1.6	0.48	3.3	7.3	0.80	0.32	0.50	1	164	15
Example 6	1.1	0.33	3.0	12.5	0.90	0.44	0.08	1	179	12
Example 7	2.5	0.48	8.7	11.1	0.85	0.36	0.05	< 1	180	12
Example 8	1.6	0.48	4.3	14.5	0.90	0.46	0.10	< 1	175	10
Example 9	1.4	0.04	5.5	0.13	0.88	0.11	1.81	< 1	160	15
Example 10	2.5	0.48	5.3	3.3	0.92	0.31	12.50	< 1	163	13
Example 11	2.5	0.48	8.5	7.4	0.54	0.35	0.07	< 1	177	10
Example 12	1.8	0.05	8.0	2.5	0.94	0.19	0.33	< 1	174	> 20
Comparative Example 1	1.1	0.33	4.5	5.9	0.83	0.52	YAP and YAM* detected	< 1	185	5
Comparative Example 2	2.5	0.48	9.0	16.6	0.30	0.61	Only YAP detected	< 1	166	1
Comparative Example 3	2.5	0.48	9.5	13.8	0.39	0.39	Only YAP detected	< 1	150	3
Comparative Example 4	2.5	0.48	4.0	the second phase did not become spherical				Only YAG detected	3	100

*YAM denotes $2Y_2O_3-Al_2O_3$

[0036]

[Effect of the Invention]

The present invention provides an AlN sintered body which has not been made available before, that is, an AlN sintered body maintaining a high-thermal conductivity and excellent in the heat resistant cycle property.

[Brief Description of the Drawings]

Fig. 1(A) is a plane view showing a front face of a copper-clad AlN sintered body sample used for a heat fatigue resistant characteristic test, and Fig. 1(B) is a plane view showing a rear face thereof.

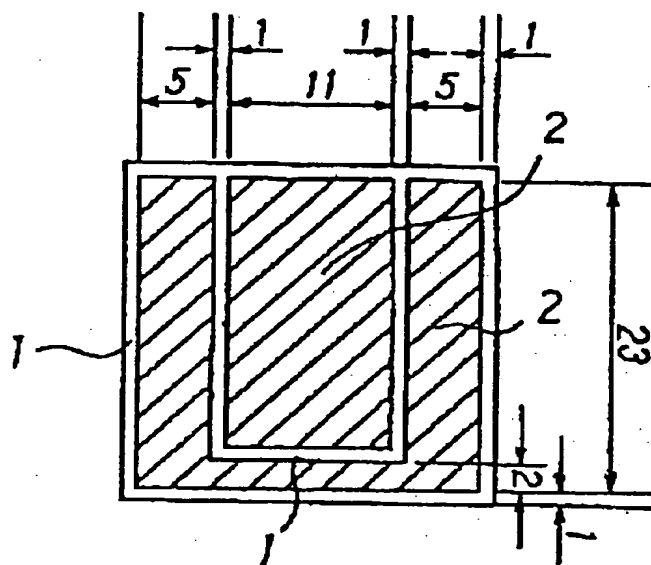
[Explanation of Symbols]

1: AlN sintered body

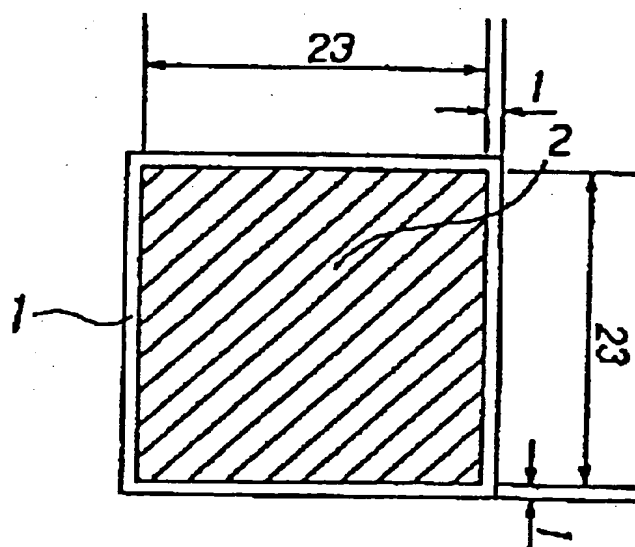
2: copper sheet

[Fig.1]

(A)



(B)



(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平6-219844

(43) 公開日 平成6年(1994)8月9日

(51) Int. Cl. ⁵

C04B 35/58

識別記号

104 D

庁内整理番号

F I

技術表示箇所

審査請求 未請求 請求項の数 2 O L (全 7 頁)

(21) 出願番号 特願平5-11740

(22) 出願日 平成5年(1993)1月27日

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(54) 【発明の名称】 A I N 焼結体およびその製造方法

(57) 【要約】

【目的】 高熱伝導率を維持し、耐熱疲労特性の優れた A I N 焼結体を提供する。

【構成】 A I N 焼結体の粒界相の組織を特定のものに制御するとともに、その組成を Y A G 相および Y A P 相にした A I N 焼結体。

【特許請求の範囲】

【請求項1】 粒界相を含有するAlN焼結体において、該焼結体切断面における粒界相の

(a) 平均周長が0.1~15 μ mで、

(b) 平均最小径と平均最大径の比率が0.5~1.0で、

(c) 平均粒径とAlN粒の平均粒径の比率が0.5以下であり、かつ該粒界相組成が3Y₂O₃・5Al₂O₃およびY₂O₃・Al₂O₃からなることを特徴とするAlN焼結体。

【請求項2】 Yの酸化物および/または炭酸塩の焼結助剤を酸化物Y₂O₃換算での焼結助剤添加量をawt%、脱脂後における酸素含量調整剤およびAlN原料粉末中に含有される酸素量をbwt%、更に脱脂後の成形体中に含有されている炭素量をcwt%としたときに

4.73b-6.30c>a>2.81b-3.75cを満足するように当該焼結助剤を、AlN原料粉末に混合し、成形、焼結することを特徴とするAlN焼結体の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、耐熱疲労特性の優れた高熱伝導性AlN焼結体に関する。

【0002】

【従来の技術】 近年、半導体工業の急速な技術革新により、IC、LSIをはじめとする大規模集積回路の高集積化、高出力化は著しく、これに伴い、パッケージ当りの発熱量は急激に増大し、基板材料の放熱性が重要視され、アルミナに替わる基板材料として熱伝導性に優れたベリリアが一部使用されているが、ベリリアは毒性が強く、取り扱い等に難点がある。そのため、アルミナやベリリアに替わる基板材料としてAlNが注目を集めている。

【0003】 AlN焼結体の助剤をはじめとして焼結体およびその製造方法については種々の先願があり、特に最近では、高熱伝導性のAlN焼結体の製法、焼結体の粒界相の組成および組織に関する出願が多い(特開昭62-52181、特開昭62-171964、特開平2-38369等)。また、AlN焼結体の熱伝導率に及ぼす微構造についてもいろいろ検討されている[第24回窯業基礎討論会要旨集P.175(1986)、日本セラミックス協会学術論文誌97[12]、1478(1989)]。また、日本セラミックス協会学術論文誌93[9]、41(1985)では、焼結助剤としてCa(NO₃)₂を添加してなる焼結体において、焼結助剤成分からなる粒界相が球状を呈することに関する知見が開示されている。

【0004】

【発明が解決しようとする課題】 上記のように最近開示されたAlN焼結体は優れた熱伝導性を有するが、高出

力化、高集積化による発熱量が増大すると、耐熱サイクル特性等の耐熱疲労特性が難点となり、基板等の薄板に亀裂が発生し、基板回路に支障をきたすという問題も出てくる。そのため、耐熱サイクル特性を向上させる必要があり、本発明はその特性を向上させることを目的とする。

【0005】

【課題を解決するための手段】 本発明者は、上記目的を解決すべく種々検討した結果、粒界相を含有するAlN焼結体において、該焼結体切断面における粒界相の

(a) 平均周長が0.1~15 μ mで、(b) 平均最小径と平均最大径の比率が0.5~1.0で、(c) 平均粒径とAlN粒の平均粒径の比率が0.5以下であり、かつ該粒界相組成が3Y₂O₃・5Al₂O₃およびY₂O₃・Al₂O₃からなることを特徴とするAlN焼結体を見出し、その焼結体の造り方としてYの酸化物および/または炭酸塩の焼結助剤を酸化物Y₂O₃換算での焼結助剤添加量をawt%、脱脂後における酸素含量調整剤およびAlN原料粉末中に含有される酸素量をbwt%、更に脱脂後の成形体中に含有されている炭素量をcwt%としたときに

4.73b-6.30c>a>2.81b-3.75cを満足するように当該焼結助剤を、AlN原料粉末に混合し、成形、焼結することを特徴とするAlN焼結体の製造方法を見出した。

【0006】 焼結助剤を用いたAlN焼結体の組織をみると、「AlN(結晶)粒」を焼結助剤が酸化物として固化した液相である「粒界相」が覆っているが、本発明者はその粒界相の覆い方およびその粒界相の存在の状態が、AlN焼結体の熱伝導率に影響を及ぼすとともに、耐熱サイクル特性等の耐熱疲労特性にも関係していることを見出した。

【0007】 これらを解析した結果、粒界相の形状、大きさおよびその組成を限定することにより、AlN焼結体の高熱伝導率を維持しつつ、耐熱疲労特性を向上することができることが分かった。すなわち、AlN焼結体において粒界相は小さく、球状で、かつその組成が3Y₂O₃・5Al₂O₃(以下YAGと略記する)およびY₂O₃・Al₂O₃(以下YAPと略記する)であることが分かった。

【0008】 それを定量的に表わすとAlN焼結体の粒界相の切断面における粒界相の平均周長が0.1~15 μ mで、平均最小径と平均最大径の比率が0.5~1.0で、平均粒径とAlN粒の平均粒径の比率が0.5以下であり、かつその組成がYAGおよびYAPであることによって高熱伝導率を維持しつつ、耐熱疲労特性が優れたAlN焼結体を得ることを本発明者は見出した。

【0009】 AlN焼結体の粒界相の切断面における粒界相の平均周長が15 μ mを超えるとAlN結晶との接触面積が大きくなり過ぎ、粒界相に大きな亀裂を生じ易

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く、焼結体の耐熱疲労特性が低下し、 $0.1\mu\text{m}$ 未満では、熱伝導率が低下し好ましくない。また、粒界相の平均最小径と平均最大径の比率が 0.5 未満であったり、粒界相の平均粒径とA1N粒の平均粒径の比率が 0.5 を超えると同様に粒界相に大きな亀裂を生じ易くA1N焼結体の耐熱疲労特性が低下する。本発明では、A1N焼結体の粒界相はA1N粒の粒界や三重点に球状に存在し、粒界相の大きさおよびA1N粒と粒界相との接触面積は非常に小さい。

【0010】次に本発明の焼結体の造り方につき工程順に説明するが、焼結助剤の添加量および酸素含量調整剤等の酸素量の関係の配合比率以外のことについては、すなわちA1N微粉末原料、バインダー等、並びに原料混合法、成形法、脱脂、焼結法のやり方やこれらの条件等は従来、通常使用されるものであり、行なわれる方法、条件で造ることができる。

【0011】主原料であるA1N微粉末は純度 95% 以上の平均粒径が $20\mu\text{m}$ 以下、好ましくは $5\mu\text{m}$ 以下の粒径を有し、金属不純物量としては 500ppm 以下のものが、また酸素含有量として $4\text{wt}\%$ 以下のものが好ましい。本発明として重要な役割を果たす焼結助剤としてはYの酸化物および/または炭酸塩を使用するが、A1N原料粉末、焼結助剤および酸素含量調整剤の総重量に対し、Yの酸化物および/または炭酸塩の焼結助剤を酸化物Y、O₂換算での焼結助剤添加量を $a\text{wt}\%$ 、脱脂後における酸素含量調整剤およびA1N原料粉末中に含有される酸素量を $b\text{wt}\%$ 、更に脱脂後の成形体中に含有されている炭素量を $c\text{wt}\%$ としたときに

$4.73b-6.30c > a > 2.81b-3.75c$ を満足するように当該焼結助剤を、A1N原料粉末に混合し、場合によっては上式を満足する範囲内で酸素含量調整剤を混合する。ここでいう「脱脂後」の脱脂については後に詳説する。

【0012】本発明の焼結助剤の添加量は、上述の式をまず満足することが重要であるが、A1N原料粉末、焼結助剤および酸素含量調整剤の総重量に対し、 $2\sim 10\text{wt}\%$ 添加することがより好ましく、更に好ましい範囲としては $2\sim 7\text{wt}\%$ である。 $2\text{wt}\%$ 未満では緻密な焼結体を得るのに長時間を要し、 $10\text{wt}\%$ を超えると熱伝導率の低下をもたらす。

【0013】本発明における酸素含量調整剤とは、上記の式に係る酸素量を調整するために添加するもので、アルミニウムの酸化物であるアルミナ Al_2O_3 または酸窒化物等を用いる。上記の式を満足し、A1N原料粉末中の酸素で足りればアルミナ等の酸素含量調整剤を添加しなくてもよい。

【0014】また、焼結前の成形体中に炭素が含まれていると、A1N原料粉末に含有されている酸素と反応するので、本発明のためには焼結助剤の添加量を減らすか、上記のアルミナ等の酸素含量調整剤の添加量が結果

として増えることになる。

【0015】A1N微粉末と焼結助剤との混合は、乾式混合または有機溶媒を使用した湿式混合により行なうが、後者の湿式混合の方がよく混合でき好ましい。混合粉末に更に、パラフィンワックス、ポリビニルブチラル、エチルセルロース等の有機バインダーを混合粉末に対し、 $3\sim 15\text{wt}\%$ 、好ましくは $5\sim 10\text{wt}\%$ 添加して、適当な成形手段、例えば乾式プレス法、ラバープレス法、押出法、射出法、ドクターブレードシート成形法等によって所定の形状に成形する。金型成形法では造粒した粉を使用するのが一般である。また、A1N焼結基板のときには、一般的には、ドクターブレード法にて成形される。この場合には、有機溶剤、ポリエチレングリコール等の分散剤、ポリビニルブチラル等のバインダーおよびブチルフタリルブチルグリコレート等の可塑剤をA1N原料粉、焼結助剤に混合し、ドクターブレード法にて薄生板（グリーンシート）を造るのが一般である。

【0016】成形後、真空、 N_2 、Arまたは大気中で $400\sim 700^\circ\text{C}$ で $0.1\sim 24$ 時間にて脱脂処理を行なう。本発明にて、添加する焼結助剤量を規定している場合の「脱脂後にこの成形体中に含有されている炭素量」とは、上記脱脂処理済の成形体を非酸化性雰囲気中または真空雰囲気中で 1300°C で2時間加熱された後に成形体中に含有されているトータルカーボン量を本発明では表わしているものとする。また、この炭素量は好ましくは $2\text{wt}\%$ 以下である。また、「脱脂後における酸素含量調整剤およびA1N原料粉末中に含有される酸素量」とは、A1N原料粉と酸素含量調整剤とを、まず真空、 N_2 、Arまたは大気中で $400\sim 700^\circ\text{C}$ で $0.1\sim 24$ 時間で熱処理後、更に非酸化性雰囲気中または真空雰囲気中で 1300°C で2時間加熱処理したときに両者内に含有されるトータル酸素量をいう。

【0017】脱脂後、 $1700\sim 2000^\circ\text{C}$ で $0.1\sim 24$ 時間にて、真空または N_2 、Ar等の非酸化性ガスの $-500\text{mmHg}\sim 10\text{kg/cm}^2$ の条件下で焼結する。上記のようにして造られた本発明のA1N焼結体のA1N（結晶）粒を覆っている粒界相は、粒界や三重点に球状に存在し、粒界相の大きさおよびA1N粒と粒界相との接触面積は非常に小さい。

【0018】また、本発明のA1N焼結体の焼結助剤成分を含有する粒界相は、ガーネット型結晶構造を有するYAGおよびペロブスカイト型結晶構造を有するYAPからなる。これらの量比を粉末X線回折（ $\text{Cu K}\alpha$ ； 40kV 、 20mA ；スキャンスピード 1deg/min ）のピーク比で見ると、YAG相、面指数（532）の回折角 $2\theta = 46.6^\circ$ の回折ピーク高さをI（YAG）と、YAP相、面指数（121）の回折角 $2\theta = 34.3^\circ$ の回折ピーク高さをI（YAP）とすると、

$0.1 < I(\text{YAG}) / I(\text{YAP}) < 3$

の範囲が好ましく、この場合には焼結助剤の添加量 a wt % の好ましい範囲は、

4.31b-5.75c > a > 2.88b-3.83c である。これらの式中の a, b, c は前述の定義と同じものである。YAG 相と YAP 相は、酸化イットリウム等の焼結助剤添加量に対する窒化アルミニウム原料粉末に含まれる酸素量が多いときに YAG 相が増え、YAP 相が減少し、逆の場合には YAG 相が減少し、YAP 相が増大する傾向がある。

【0019】

【実施例】以下、実施例にて本発明を詳細に説明する。

実施例 1

まず、焼結に使用する AlN 原料粉末について本発明で定義する脱脂後の含有酸素量および成形体中の含有炭素量を求めた。すなわち、Al 直接窒化法による市販の AlN 原料粉末 (酸素含有量 1.1 wt %, 平均粒径 1.5 μm, Fe 60 ppm, Si 100 ppm, Mg < 30 ppm) 100 重量部に成形用バインダーとしてポリプロピレングリコール 1 重量部とポリビニルブチラール 5 重量部、可塑剤としてジブチルフタレート 5 重量部、溶剤としてブタノール 27 重量部を加え、ナイロン製ボールミルボットで 48 時間混合し、スラリーを調整した。このスラリーを真空脱泡した後、ドクターブレード法にてシート成形し乾燥した。そして、厚さ 0.75 mm で得られたシートを 30 mm 角の形状に打ち抜き、大気中で 550℃ にて 6 時間の条件で脱脂した。この脱脂体を更に窒素中に 1300℃ で 2 時間の条件で加熱処理した。この加熱処理成形体の含有酸素量と含有炭素量を測定したところ、それぞれ 1.4 wt %, 0.04 wt % であった。この場合、酸素含有調整剤は含まれておらず、また、AlN 原料粉末以外のポリプロピレングリコール等は 1300℃ では酸素は残らないことを確認しているため、上記の脱脂後の成形体中の含有酸素量の値はそのまま、本発明で定義する脱脂後における酸素含有調整剤 (実施例 1 では無添加) および AlN 原料粉末中に含有される酸素量 b wt % に相当する。

【0020】次に、上記と同じ AlN 原料粉末に Y₂O₃ (日本イットリウム社製微粉末製品、純度 99.9 %、平均粒径 0.4 μm) 粉 5 wt % を加えた混合粉末 100 重量部に、前述と全く同じ成形用バインダー、可塑剤および溶剤をそれぞれについて前述と同一量加えて、同様な方法にて厚さ 0.75 mm のグリーンシートを造った。得られたシートを 30 mm 角のサイズに打ち抜き、大気中で 550℃ で 6 時間の条件で脱脂した。脱脂後、窒化ホウ素微粉末を塗布した該脱脂体を 10 枚積み重ね、窒化ホウ素製容器に収納して、真空焼結炉内で大気圧の窒素気流 (N₂ ガス流量 100 リットル/hr) 中 1830℃ で 16 時間の条件で焼結した。得られた焼結体の組織等を観察するために、焼結体を切断し、切断面を研磨し、SE

長」、「平均最小径と平均最大径の比率」および「粒界相の平均粒径と AlN 粒の平均粒径の比率」を求めた。

【0021】粒界相の「平均最小径と平均最大径の比率」が 0.5 より小さい、すなわち粒界相の形状が球状になっていないことが分り、再度大気圧の窒素気流中、1825℃ で 16 時間焼結した。得られた焼結体の組織を同様な方法で評価した結果を表 1 に示す。また、当該焼結体をそれぞれ微粉砕し、粉末 X 線回折用試料となし、I (YAG) / I (YAP) 値の測定を行なった。

10 この際の測定の装置は理学電機社製ガイガーフレックス RAD-2B、測定条件の主なものはこの通りの条件である。

ターゲット	Cu Kα
電圧、電流	40 kV, 20 mA
スキャンスピード	1 deg/min
スリット	1-0.3-1

【0022】次に、当該焼結体の表面を湿式ブラスト処理して、表面に析出していた焼結助剤を除去した。ブラスト処理には、#320 の炭化ケイ素砥粒を使用した。20 表面をブラスト処理した焼結体を用い、下記の方法で図 1 の寸法にて銅張り基板を作製し、耐熱疲労特性を測定した。銅張りの接合材料としては、粒径が 5~20 μm の Cu 粉末 84.5 重量部、粒径が 5~10 μm の Ag 粉末 1.4 重量部、粒径が 5~10 μm の Ti 粉末 1.5 重量部を混合した金属粉末 85 wt % に、テキサノール中にバインダーとしてエチルセルロース 12 % を配合したビークル 15 wt % を混練し、ペースト状としたものを準備した。このペースト状接合材料を窒化アルミニウム焼結体にスクリーン印刷法を利用して 35 μm の厚さに塗布した。この際、回路側はパターン部分にのみ、ヒートシンク側はヒートシンク部全面に、それぞれ塗布した。次に、塗布した窒化アルミニウム焼結体を 600℃ で 5 分、30 分プロファイルで乾燥し脱脂して、銅板を重ね合わせて 850℃ で 5 分加熱して接合した。次に、回路パターン側の銅板表面にレジストを塗布した。レジストは、パターンとなる部分の周囲より 200 μm 大きくなるように、スクリーン印刷法により塗布した。また、ヒートシンク側の銅板には全面にわたってレジストを塗布した。

40 【0023】レジスト塗布後、温度 39℃ の塩化第二鉄溶液をスプレー噴霧し、レジストを塗布しない不要銅板部分を除去し、水洗し乾燥して銅張り基板を得た。そして、銅張り基板の耐熱疲労特性を評価した。耐熱疲労特性評価試験は、窒素中で室温から 400℃ まで 10 分で昇温し、400℃ で 5 分間保持して、再度室温に戻す加熱冷却方法を用いた。そして、焼結体にクラックが発生するまでのサイクル数を調べた。その結果、耐熱疲労特性が従来になく極めて優れていることが分かった (耐熱疲労特性評価結果は表 1 に示す)。更に、焼結体の開気孔を水で 3 時間煮沸し、その飽水重量より求め、表 1 に

併記した。また、熱伝導率は熱サイクルテストに用いた焼結体につき、レーザーフラッシュ法により求め、表1に併記した。

【0024】実施例2

実施例1と同じAlN原料粉末を純度99.9%の15~20mmφのアルミナボールにて水溶媒湿式ボールミル粉碎し、平均粒径1.1μmまで粉碎したAlN原料粉末を使用した。この場合、脱脂後の酸素含量b値はAl₂O₃も混入したためか1.8wt%であった。この点とY₂O₃添加量が6wt%である点と焼結温度が1820℃

(保持時間は同じ16時間)であることを除いては、実施例1と全く同じ条件等で焼結体を得た。その後の焼結体組織等の結果、I(YAG)/I(YAP)値、耐熱疲労特性等を求め、表1に示した。

【0025】実施例3

未粉碎のAlN原料粉末で酸素含有量が2.5wt%で、脱脂後のb値も2.5wt%であるAlN原料粉末(他の平均粒径、不純物量も実施例1の原料と同一)を用いたこととY₂O₃添加量が6.2wt%である点と焼結前の脱脂条件が真空(1×10⁻¹Torr)にて680℃で2時間である点および焼結温度が1825℃(時間は16時間で同じ)である点を除いて他の条件等は実施例1と全く同じで処理して焼結体を得た。該焼結体の特性等を表1に示す。

【0026】実施例4

Y₂O₃添加量を5.8wt%にしたこと以外は実施例3と全く同じ処理にて焼結体を造り、表1に示す特性等の結果を得た。

【0027】実施例5

未粉碎AlN原料粉末で酸素含有量が1.6wt%で、脱脂後のb値も1.6wt%である点とY₂O₃添加量が3.3wt%である点を除けばその他は実施例3と全く同じにて焼結体を造り、表1に示す結果を得た。

【0028】実施例6

還元窒化法による市販のAlN原料粉末(酸素含有量1.1wt%、平均粒径1.4μm、Fe60ppm、Si30ppm、Mg<5ppm)で脱脂後のb値も1.1wt%であるAlN原料粉末を使用し、Y₂O₃添加量が3.0wt%で、焼結条件を室素中で1825℃で16時間後、更に室素中1805℃で16時間焼結したこと以外は実施例3と全く同様にし、焼結体を造り、表1の結果を得た。1825℃で16時間の焼結段階では焼結体は粒界相の平均最小径と平均最大径の比率が0.2以下、すなわち形状が球状となっていないものと球状のものとが混じり合っていた。

【0029】実施例7

Y₂O₃添加量を8.7wt%としたこと以外、実施例3と同様に焼結体を作製し、銅板を接合して基板を得た。そして、実施例1と同様に基板の耐熱疲労特性を評価し

た。その結果、耐熱疲労特性も従来になく極めて優れて

いることが分かった(耐熱疲労特性評価結果は表1に示す)。

実施例8

Y₂O₃添加量を4.3wt%としたこと以外、実施例5と同様に焼結体を作製し、銅板を接合して銅張り基板を得た。そして、実施例1と同様に基板の耐熱疲労特性を評価した。その結果、耐熱疲労特性も従来になく極めて優れていることが分かった(耐熱疲労特性評価結果は表1に示す)。

10 実施例9

Y₂O₃添加量を5.5wt%としたこと以外、実施例1と同様に焼結体を作製し、銅板を接合して銅張り基板を得た。そして、実施例1と同様に基板の耐熱疲労特性を評価した。その結果、耐熱疲労特性も従来になく極めて優れていることが分かった(耐熱疲労特性評価結果は表1に示す)。

【0030】実施例10

Y₂O₃添加量を5.3wt%としたこと以外、実施例3と同様に焼結体を作製し、銅板を接合して銅張り基板を得た。そして、実施例1と同様に基板の耐熱疲労特性を評価した。その結果、耐熱疲労特性も従来になく極めて優れていることが分かった(耐熱疲労特性評価結果は表1に示す)。

実施例11

Y₂O₃添加量を8.5wt%としたこと以外、実施例3と同様に焼結体を作製し、銅板を接合して銅張り基板を得た。そして、実施例1と同様に基板の耐熱疲労特性を評価した。その結果、耐熱疲労特性も従来になく極めて優れていることが分かった(耐熱疲労特性評価結果は表1に示す)。

【0031】実施例12

実施例1と同一の窒化アルミニウム粉99.15wt%に酸素調整剤として高純度アルミナ粉末(昭和電工製 純度99.9%)0.85wt%を添加した。この場合、脱脂後におけるbおよびcの値は、それぞれ、1.8wt%、0.05wt%であった。上記の酸素調整剤を添加した窒化アルミニウム粉末に対してY₂O₃6wt%を加え、実施例2と同様に成形、脱脂、焼結し、本発明の目的とする焼結体を得た。得られた焼結体表面の析出助剤相を除去し、実施例1と同様に銅張り基板の耐熱疲労特性を評価した。その結果、耐熱疲労特性が表1に示すように従来になく優れていることが分かった。

【0032】比較例1

実施例6においてY₂O₃添加量を4.5wt%とし、焼結温度を1805℃である点を除けば実施例6と全く同じ条件で焼結体を造り、表1に示す結果を得た。

比較例2

Y₂O₃添加量を9.0wt%としたこと以外、実施例3と同様に焼結体を作製した。次に、焼結体表面の析出助剤相を除去した後、実施例1と同一のペースト状接合材料

を使用して銅板を接合し、銅張り基板を得た。そして、実施例1と同様に基板の耐熱疲労特性を評価した。その結果、加熱冷却サイクル1回目で焼結体にクラックが発生し耐熱疲労特性に劣ることが分かった（耐熱疲労特性評価結果は表1に示す）。

【0033】比較例3

Y₂O₃添加量を9.5wt%としたこと以外、実施例3と同様に焼結体を作製した。次に、焼結体表面の析出助剤相を除去した後、実施例1と同一のペースト状接合材料を使用して銅板を接合し、銅張り基板を得た。そして、実施例1と同様に基板の耐熱疲労特性を評価した。その結果、加熱冷却サイクル3回目で焼結体にクラックが発生し耐熱疲労特性に劣ることが分かった（耐熱疲労特性評価結果は表1に示す）。

比較例4

Y₂O₃添加量を4.0wt%としたこと、および焼結温度を1850℃×16Hrとしたこと以外、実施例3と同様に焼結体を作製した。次に、焼結体表面の析出助剤相を除去した後、実施例1と同一のペースト状接合材料を使用して銅板を接合し、銅張り基板を得た。そして、実施例1と同様に基板の耐熱疲労特性を評価した。その結果、加熱冷却サイクル3回目で焼結体にクラックが発生し耐熱疲労特性に劣ることが分かった（耐熱疲労特性評価結果は表1に示す）。

【0034】上記のいろいろな結果より分かるように実施例で得られたように高熱伝導率を維持し、熱サイクルテストにて良結果を得たものは比較例では得られなかった。

【0035】

【表1】

	脱脂後		Y ₂ O ₃ 添加量 (wt%)	粒界相 の平均 周 長 (μm)	粒 界 相 の (平均最小径) (平均最大径) 比 率	(粒界相の平均粒径) (A & N の平均粒径) 比 率	I (YAG) I (YAP)	A & N 焼 結 体		
	酸 素 量 b (wt%)	炭 素 量 c (wt%)						気孔率 (%)	熱伝導率 (W/m · k)	耐熱疲労特性 サイクル (回数)
実施例 1	1.4	0.04	5.0	6.1	0.89	0.28	1.11	< 1	161	18
実施例 2	1.8	0.05	6.0	2.5	0.85	0.18	0.30	< 1	172	> 20
実施例 3	2.5	0.48	6.2	4.7	0.92	0.24	0.40	< 1	167	> 20
実施例 4	2.5	0.48	5.8	4.7	0.95	0.27	2.50	< 1	155	> 20
実施例 5	1.6	0.48	3.3	7.3	0.80	0.32	0.50	1	164	15
実施例 6	1.1	0.33	3.0	12.5	0.90	0.44	0.08	1	179	12
実施例 7	2.5	0.48	8.7	11.1	0.85	0.36	0.05	< 1	180	12
実施例 8	1.6	0.48	4.3	14.5	0.90	0.46	0.10	< 1	175	10
実施例 9	1.4	0.04	5.5	0.13	0.88	0.11	1.81	< 1	160	15
実施例 10	2.5	0.48	5.3	3.3	0.92	0.31	12.50	< 1	153	13
実施例 11	2.5	0.48	8.5	7.4	0.54	0.35	0.07	< 1	177	10
実施例 12	1.8	0.05	6.0	2.5	0.94	0.19	0.33	< 1	174	> 20
比較例 1	1.1	0.33	4.5	5.9	0.83	0.52	YAP, YAM を 検 出	< 1	185	5
比較例 2	2.5	0.48	9.0	18.6	0.30	0.61	YAP のみ	< 1	166	1
比較例 3	2.5	0.48	9.5	13.8	0.39	0.39	YAP のみ	< 1	150	3
比較例 4	2.5	0.48	4.0	第二相が球状とならなかった			YAG のみ	3	100	1

*YAMは2Y₂O₃・A₂O₃である。

【0036】

【発明の効果】本発明により従来にないA1N焼結体すなわち、高熱伝導率を維持し、かつ、耐熱サイクル特性の優れたA1N焼結体を得られた。

【図面の簡単な説明】

【図1】耐熱疲労特性試験に使用した銅板張りA1N焼

40 結体試料の平面図である。(A)が表面、(B)が裏面である。

【符号の説明】

- 1 A1N焼結体
- 2 銅板

【図 1】

